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(54) Title: FISCHER-TROPSCH CATALYSTS

(57) Abstract: A method of producing an alumina-supported catalyst for use in a Fischer-Tropsch synthesis reaction, which com-  
prises: calcining an initial  $\gamma$ -alumina support material at a temperature of at least 550°C to produce a modified alumina support  
material; impregnating the modified alumina support material with a source cobalt; calcining the impregnated support material at a  
temperature of 700°C to 1200°C, and activating the catalyst.

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## Fischer-Tropsch Catalysts

The present invention relates to supported catalysts and their use in Fischer-Tropsch synthesis reactions, and more specifically to processes for the production of the catalyst and support, and to the catalyst and support themselves.

Conversion of natural gas to liquid hydrocarbons ("Gas To Liquids" or "GTL" process) is based on a 3 step procedure consisting of: 1) synthesis gas production; 2) synthesis gas conversion by FT synthesis; and 3) upgrading of FT products (wax and naphtha/distillates) to final products.

The Fischer-Tropsch reaction for conversion of synthesis gas, a mixture of CO and hydrogen, possibly also containing essentially inert components like CO<sub>2</sub>, nitrogen and methane, is commercially operated over catalysts containing the active metals Fe or Co. Iron catalysts are best suited for synthesis gas with low H<sub>2</sub>/CO ratios (< 1.2), e.g. from coal or other heavy hydrocarbon feedstock, where this ratio is considerably lower than the consumption ratio of the FT-reaction (2.0 – 2.1). The present invention is concerned with Co-based catalysts, in particular, supported Co-based catalysts. A variety of products can be made by the FT-reaction, but from supported cobalt, the primary product is long-chain hydrocarbons that can be further upgraded to products like diesel fuel and petrochemical naphtha. Byproducts can include olefins and oxygenates.

To achieve sufficient catalytic activity, it is customary to disperse the Co on a catalyst carrier, often referred to as the support material. In this way, a larger portion of Co is exposed as surface atoms where the reaction can take place. The present invention is concerned with alumina, as a support material.

Supported cobalt catalysts are the preferred catalysts for the FT synthesis. The most important properties of a cobalt FT catalyst are the activity, the selectivity usually to C<sub>5+</sub> and heavier products and the resistance towards deactivation.

5 Known catalysts are typically based on titania, silica or alumina supports and various metals and metal oxides have been shown to be useful as promoters.

In a paper by Iglesia et al. ["Selectivity Control and Catalyst Design in the Fischer-Tropsch Synthesis: Sites, Pellets and Reactors" Advances in Catalysis, Vol 3, 1993] a Thiele modulus is defined as a product of two components,  $\Psi_n$  and  $\chi$ , where  $\Psi_n$  depends only on the diffusivity and reactivity of the individual molecules, whereas  $\chi$  depends only on the physical properties and site density of the catalyst. They have described a model whereby the selectivity to C<sub>5+</sub> products can be described as a volcano plot in terms of  $\chi$ . The structural parameter is given as:

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$$\chi = R_o^2 \Phi \theta_m / r_p ,$$

where  $\theta_m$  is the site density, e.g. as the number of surface atoms of Co metal atoms per cm<sup>2</sup> of pore area in the catalyst particle,  $R_o$  is the diffusion length, i.e. the radius of an essentially spherical catalyst particle,  $\Phi$  is the porosity of the particle (cm<sup>3</sup> pore volume/cm<sup>3</sup> particle volume) and  $r_p$  is the mean pore radius.

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25 This expression suggests that  $\chi$  only depends on universal constant, characteristic data for cobalt in the catalyst as well as the size and density of the catalyst particles. It is particularly significant that  $\chi$  does not depend on the pore radius,  $r_p$ . However, it now appears that the selectivity of the Fischer-Tropsch reaction to C<sub>5+</sub> products indeed does in fact depend on the pore size.

In a paper by Saib et al. ["Silica supported cobalt Fischer-Tropsch catalysts: effect of pore diameter of support" Catalysis Today 71 (2002) 395-402], the influence of the effect of the average pore diameter of a silica support on the properties of a cobalt catalyst and their performance in F-T synthesis is discussed. The article concludes that the support pore diameter has a strong effect on cobalt crystallite size with larger crystallites forming in larger pore sizes. Also, the activity was found to be a function of the metal dispersion and the maximum C<sub>5+</sub> selectivity a function of the conversion.

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In EP 1 129 776 A1 it is argued that internal diffusion phenomena in a catalyst particle depend on the chemical and morphological structure of the catalyst (pore dimensions, surface area, density of the active sites) and on the molecular dimensions of the species in question. This is a general teaching found in relevant textbooks, e.g. expressed in terms of the Thiele modulus, and it is significant that the pore dimension, i.e. the pore radius or diameter is one of the critical parameters. Further, it is taught that for the Fischer-Tropsch synthesis, interparticle diffusion will create low concentrations of CO towards the centre of the particle with a consequent progressive rise in the H<sub>2</sub>/CO ratio inside the catalyst and that this condition favours the formation of light hydrocarbons (lower  $\alpha$ -value and C<sub>5+</sub> fraction). On the other hand, it is stated that multiphase reactors of the slurry type generally use small catalyst particles (20 - 150  $\mu$ m) which do not give internal diffusion problems, and more specifically that for catalysts based on differently supported cobalt used in the Fischer-Tropsch synthesis, it is possible to neglect internal diffusion limitations by operation with particles having diameter of less than 200  $\mu$ m.

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In EP 0 736 326 B1, it is shown that the C<sub>5+</sub> selectivity can increase over a certain range of increasing pore size for a cobalt on alumina type FT catalyst.

However, no reference or details of the method of measuring pore size is given, and it is well known that reported values vary significantly with method, e.g. for different probe gases or whether adsorption or desorption isotherms are employed.

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In general, after impregnation of an alumina carrier with a solution of a cobalt catalyst material, the carrier is dried and calcined at a relatively low temperature of 200 to 450°C, eg. at 300°C, for 2 to 16 hours. However, it is known that prolonged calcination at higher temperatures, eg. above 500°C can  
10 reduce catalyst activity.

This is in the first instance due to agglomeration of Co crystallites giving a reduced Co surface area for the FT-reaction, but at higher temperatures Co reacts with the alumina itself to form an inactive spinel phase, cobalt aluminate  
15  $\text{CoAl}_2\text{O}_4$ . Transformation to cobalt aluminate was demonstrated by Davis and co-workers (Applied Catalysis, Volume 247, Pages 335-343, 2003) to occur at 650°C and to transform completely at 850°C. The present invention relates to the surprising beneficial effect of high temperature treatment of an impregnated catalyst carrier on its attrition level.

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According to one aspect of the invention, there is provided a method of producing an alumina-supported catalyst, which comprises the following steps: a first impregnation step in which an initial alumina support material is impregnated with a source of a 2-valent metal capable of forming a spinel  
25 compound with alumina; a first calcination step in which the impregnated alumina support material is calcined at a temperature of at least 550°C to produce a modified alumina support material; a second impregnation step in which the modified alumina support material is impregnated with a source of catalytically active metal; and a second calcination step in which the

impregnated modified support material is calcined at a temperature of at least 150°C.

5 According to another aspect of the invention, there is provided a method for the production of an alumina support for a catalyst, which comprises impregnating an initial alumina support material with a source of a 2-valent metal capable of forming a spinel compound with alumina, and calcining the impregnated alumina at a temperature of at least 550°C.

10 The invention also extends to catalyst material made in accordance with the first aspect and a support material made in accordance with the second aspect.

The invention also extends to the use of the support material and the use of the catalyst in an F-T synthesis.

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The F-T synthesis may be conducted in a fixed bed reactor or a non-fixed bed reactor, such as a slurry bubble column.

20 The invention also extends to a process for the production of hydrocarbons which comprise subjecting H<sub>2</sub> and CO gases to a Fischer-Tropsch synthesis reaction in a reactor in the presence of a catalyst of the invention. The process can be conducted under typical F-T operating conditions. The products can be subjected to various post-processing operations, such as de-waxing, hydro-isomerisation and/or hydro-cracking.

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Amorphous catalyst support materials typically have specific surface areas between 50 and 500 m<sup>2</sup>/g, more typically between 100 and 300 m<sup>2</sup>/g. The starting alumina materials used in the present invention are all, at least predominantly, of the  $\gamma$ -alumina type, preferably with specific surface areas

between 150 and 200 m<sup>2</sup>/g. These supports can be prepared by spray-drying techniques of an appropriate solution in order to obtain essentially spherical particles of appropriate size, e.g. 80 % in the range between 30 – 120 µm. After spray-drying, the material is calcined at a high temperature to give the appropriate crystal size and pore structure.

It is also important that the total pore volume is sufficiently high, above 0.2 cm<sup>3</sup>/g or better, above 0.4 cm<sup>3</sup>/g, or even above 0.6 cm<sup>3</sup>/g. The pore volume is often measured by the BET method applying nitrogen as the adsorption gas.

This method does not take into account large pores where a mercury porosimeter is more relevant. A less accurate, but more practical parameter is the measured water absorbtivity, which can be directly correlated with the amount of cobalt that can be impregnated on the catalyst by the incipient wetness procedure. A high pore volume will give a light material suitable for operation in a slurry environment and ease the impregnation by minimising the number of impregnation steps required. At the same time the support, and the final catalyst, should have sufficient strength for extended operation of months and years with minimal attrition of the materials. This can be tested in a slurry environment or by the ASTM method applicable for testing FCC (fluid catalytic cracking) catalysts.

The properties of γ-alumina catalyst support materials have been investigated, both as received from the alumina vendor (Sasol GmbH of Hamburg, Germany), and following heat treatment. The properties are set out in Table 1.

Table 1. Properties of alumina as received and heat treated.

Alumina batch no.	Calcination temperature [°C]	Surface area [m <sup>2</sup> /g]	Pore volume(N <sub>2</sub> ) [ml/g]	Pore diameter [nm]	Attrition [g/50g at 5h]	Water absorbitivity [ml/g]**	α-alumina [%]
Al-1	500*	191	0,721	11,4	4,9	1,23	0
"	1100	55	0,390	22,0	7,0	0,85	17
"	1130	15	0,084	20,4	15,2	0,69	85
"	1150	7	0,019	11,4	39,0	0,60	
Al-2	500*	170	0,734	12,9	4,8	1,30	0
"	900	107	0,684	19,1	4,9	1,15	
"	1100	56			6,9	0,85	
"	1130	18	0,108	22,2		0,75	87
"	1140	10	0,049	18,3	26,3	0,71	97
"	1140	7	0,026	14,8	26,0	0,74	100

\* Equivalent to "as received" material. The average particle size is respectively 62 µm and 59 µm.

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\*\* The water absorbitivity is determined as the "incipient wetness" point by successively adding water to the point where water is visually released from the pores of the alumina by gentle tapping of the beaker containing the material.

10 The as received γ-alumina materials from the alumina vendor have been treated in one or both of two ways, namely, further heat treatment/calcinations at temperatures in the range 500 – 1200 °C; and impregnation by one or a mixture of substances followed by heat treatment in the 700 – 1300°C temperature range. The properties of the resulting materials have been

15 investigated.



Upon high temperature treatment, the  $\gamma$ -aluminas or the different alumina hydrates will be converted to transition phase aluminas, denoted  $\delta$ ,  $\theta$ ,  $\eta$ ,  $\chi$  or  $\kappa$  - aluminas, that all finally will be converted to  $\alpha$ -alumina, with a gradual decrease in specific surface areas. These aluminas may also be suitable as support materials for cobalt for the Fischer-Tropsch synthesis, even though this may have specific surface areas in the range 10 – 50 m<sup>2</sup>/g. The specific surface areas and pore volumes must be balanced towards the requirements for sufficiently high cobalt metal loading and dispersion. However, it is also possible to increase the high temperature surface stability of aluminas by adding certain stabilising agents like lanthanum (lanthanum oxide). In this way, the  $\gamma$ -phase can be retained, even above 1000 °C. Other stabilising agents have been used, such as magnesia and ceria.

Three other properties are important for the support, and for the final catalyst, in particular when used in a slurry reactor environment such as a slurry bubble column. These are the particle density, the particle size, and the abrasion or attrition resistance. The density is important in order to achieve a suitable distribution (dispersion) of the catalyst particles in the reactor. A light material is particularly advantageous for avoiding catalyst settling or an excessive concentration of particles in the lower part of the reactor. The particle size also affects settling and the catalyst concentration profile, but should not be excessively small, since this makes separation of the liquid product from the reactor slurry more difficult and increases the incidence of particles being transported with the gas phase at the top of the reactor. Attrition should be minimised to prolong the life of the catalyst and to avoid contamination of the liquid hydrocarbon product.

Examples of these parameters for selected  $\gamma$ -alumina supports and their heat-treated analogues are given in Table 1. As can be seen, there is a clear

tendency for the attrition resistance to diminish significantly as the calcination temperature exceeds 1100°C simultaneously with an increase of the  $\alpha$ -alumina content. It is stated in WO 02/47816 that catalysts with low surface areas and/or high  $\alpha$ -alumina contents lead to a significant increase in the selectivity to the desired C5+ products in the FT-synthesis. As seen, however, the pore volume is reduced and attrition can reach an unacceptable level.

As mentioned above, an important method for characterisation of the present catalysts and support materials is related to the determination of the pore characteristics; pore volume, pore size distribution, surface area and average pore size. Various techniques may be applied, but most are variations of the so-called BET method using the adsorption or desorption isotherms of a gas that is adsorbed to the surface of the pores, typically nitrogen, but also certain noble gases or mercury are used for specialised purposes. In the present invention, the nitrogen desorption isotherm is used, measured by standard procedures on an ASAP 2000 instrument from Micromeritics and the standard included software for calculation of the pore characteristics.

The values reported in the Tables in this specification are the BET surface area, the BJH desorption cumulative pore volume between 17 and 3000 Å diameter and the BJH desorption average pore diameter (4V/A). Specific values will vary depending on the method, but the general findings are expected to be valid independent of the method employed, and characterisation data compared therefore should be harmonised to a given method.

The modified ASTM type equipment for testing attrition consists of two main parts, one air feeding system and one reactor where the attrition takes place. Compressed air passes through a pressure regulator (5 bar) to a moisture chamber where the air is moistened to approximately 30 % relative moisture.

This is done to avoid static electricity in the system. The amount of air is then adjusted in a mass flow controller. The humid air then enters the reactor through a sieve tray where the holes have a diameter of 0.4 mm. Because of these holes, the gas reaches sonic velocity, which causes the “wear and tear” on the particles in the reactor. The reactor has an internal diameter of 35.6 mm (1.4 inches) and a length of 711 mm (28 inches) and the pressure is approximately 1.8 bar. After passing through the reactor, the velocity is lowered in a separation chamber which has an internal diameter of 112 mm (4.4 inches) and a length of 305 mm (12 inches). There is a conical connection 203 mm long (8 inches) between the reactor and the separation chamber.

Particles  $> 40 \mu\text{m}$  will fall back down into the reactor, while smaller particles  $< 40 \mu\text{m}$  (fines) will enter a Soxhlet-filter through a u-formed tubing, connected to the separation chamber via a conical connection 106 mm long (4 inches). A vibrator is mounted on the separation chamber, to loosen any particles on the inside walls.

50 g of powder or catalyst, sieved to  $> 40 \mu\text{m}$  before testing, is loaded to the reactor, and the reactor is connected to the separation chamber. The air is turned on, and the fines produced in the reactor and collected in the Soxhlet filter are weighed every 15 minutes during the first 2 hours, and every 30 minutes during the next 3 hours. A normal run lasts 5 hours and the amount of fines produced can be plotted against time.

## **Support modification and catalyst preparation**

Table 2. Properties of alumina modified by metal salt impregnation and high-temperature treatment. Al-2 is the starting material.

Impregnated metal and level [wt%]*	Calcination temperature [°C]	Surface area [m <sup>2</sup> /g]	Pore volume(N <sub>2</sub> ) [ml/g]	Pore diameter [nm]	Attrition [g/50g at 5h]**	α-alumina [%]***	Water absorbitivity (ml/g)
5 Co	900	107	0,62	18	4,3		1,00
"	1050	44	0,30	23	4,6		0,74
	1100	12	0,07	23	12		0,61
"	1140	9	0,05	22	20		
10 Co	900	100	0,61	18	4,5		1,00
"	1050	47	0,34	24	4,8		0,70
"	1100	14	0,15	40	5,5		0,54
"	1140	10	0,09	33	6,9		0,50
20 Co	300	144	0,49	11	6,8		0,92
"	900	76	0,47	20	7,0	0	0,90
"	1140	10	0,09	33	3,4	12	0,47
10 Al	900	90	0,42	14	8,8		1,12
"	1050	55	0,34	18	5,0		0,80
"	1140	6	0,02	15	28,0		0,78
10 Zn	1120	17	0,16	36	10,5	54	0,57
"	1140	12	0,13	38	6,9	63	0,56
"	1160	11	0,11	37	6,9	64	0,53
12,5 Zn	1140	14	0,16	39	4,6		0,52
15 Zn	1140	13	0,15	42	3,4		0,47
5 Mg	1140	17	0,16	32	3,0		0,56
10 Mg	1120	36	0,21	18			0,57
"	1140	29	0,18	19	0,3	21	0,51
"	1160	16	0,12	22	0,5	37	0,41
5Mg+5Zn	1140	15	0,14	32	0,5		0,70

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10 Mn	1140	3	0,01	12	16,4		0,53
3 Ni	1140	9	0,07	28	<b>6,2</b>		0,50
5 Ni	1140	13	0,10	27	<b>3,6</b>	78	0,5
"	1150	10	0,09	33			0,5
"	1160	8	0,04	20			0,5
"	1170	9	0,06	27			0,5
"	1180	8	0,05	21	<b>3,0</b>		0,45
5 Ni****	1140	18	0,15	29	<b>2,9</b>		0,50
7,5Ni****	1120	31	0,21	19	<b>1,4</b>	37	0,51
7,5 Ni	1140	20	0,17	28	<b>2,8</b>	57	0,51
10 Ni	900	93	0,38	14			
10 Ni	1140	18	0,165	30	<b>1,5</b>		0,45

\* Nominal values assuming complete reduction to metal. Note that the samples here all are in oxide form.

\*\* Bold face signifies lower attrition than the alumina carrier calcined at the same temperature.

\*\*\*Simplified estimation from peak heights of most intense peak for each compound in standard Cu-XRD. The other XRD peaks for the samples calcined at 1140°C correspond to the  $\text{MeAl}_2\text{O}_4$  spinel.

\*\*\*\* On Al-1 type alumina.

From Table 2 it can be seen that a standard catalyst in calcined form, (the 20Co/300 °C sample), has an attrition level higher than the support material, that is to say, 6.8 g compared to 4.8 g. In other words, a significant reduction in strength is observed by impregnation of cobalt nitrate and standard calcination. What has now been astonishingly found is that the strength increases significantly by further calcination to 1140 °C (3.4 g), an attrition level which is actually lower than for the starting alumina material. The

comparison is even more compelling with the alumina support calcined at the same temperature (1140°C), as most of the strength then is lost (26.3 g). The positive effect on the catalyst strength increases with calcination temperature and Co loading.

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For comparison, impregnation of aluminium nitrate was attempted, but it can be seen that little effect on the attrition was gained as in fact the attrition level of 28.0 g for the impregnated sample is slightly above the 26.3 g obtained for the support, both calcined at 1140 °C. On the other hand, Zn has a positive effect on attrition, very much in line with Co. It therefore seems as if impregnation with a metal salt and high temperature calcination enhances the strength of alumina if the added metal is able to form a well defined crystalline mixed oxide with aluminium, in this case a spinel with composition  $\text{MeAl}_2\text{O}_4$ , Me being a 2-valent metal. An even stronger effect is found using an Mg salt, as an extremely strong material is formed. The attrition level after 5 h in a jet cup of 0.5 % is below anything seen for a catalyst or catalyst support. The origin of the effect can only be speculative, but it would seem that the magnesium ion is smaller than  $\text{Co}^{2+}$  or  $\text{Zn}^{2+}$  and therefore may exhibit higher solid-state diffusion rates at the given temperature. This points to a possible positive effect of modifying alumina with other metal salts/oxides containing small metal ions, like lithium. Nevertheless, it was surprisingly found that nickel gives a very attrition resistant modified alumina support, approaching the values for magnesium (Figure 1).

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Unless otherwise stated, all the catalysts used contain a nominal amount of cobalt of 20 wt% and 0,5 wt% Re, calculated assuming reduced catalysts with complete reduction of cobalt. The actual metal loading as determined by XRF or ICP may vary up to  $\pm 10\%$ , i.e. for cobalt between 18 and 22 w% of the total reduced catalyst weight. Other promoters besides rhenium, specifically,

platinum, iridium or ruthenium, can be employed. It is also possible to add a second promoter such as lanthanum oxide or a mixture of oxides of the lanthanides or other compounds which are difficult to reduce.

5 Before impregnation, the catalyst support may be precalcined at about 500 °C. Impregnation is usually in one step, but multiple steps can also be employed, from a mixed aqueous solution of appropriate metal salts, generally of cobalt nitrate and perrhenic acid or alternatively ammonium perrhenate. The  
10 impregnation technique generally used is the pore filling or "incipient wetness" method, in which the solution is mixed with the dry support until the pores are filled. The definition of the end point of this method may vary somewhat from laboratory to laboratory so that an impregnated catalyst could have a completely dry appearance or a sticky snow-like appearance. However, in no instances are there any free flowing liquid present.

15 A number of alternative impregnation procedures are known in the art which use alternative solvents and chemicals, however, in the present invention, the preferred procedure involves aqueous incipient wetness with solutions of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ) and perrhenic acid ( $\text{HReO}_4$ ). Possible alternatives  
20 include using cobalt acetate(s), cobalt halide(s), cobalt carbonyl(s), cobalt oxalate(s), cobalt phosphate(s), organic cobalt compounds, ammonium perrhenate, rhenium halide(s), rhenium carbonyl(s), industrial metal salt solutions, organic solvents, etc. Furthermore, the impregnation technique may encompass all available methods besides incipient wetness, such as  
25 precipitation, impregnation from slurry with surplus liquid, chemical vapour deposition etc. It is well known that the impregnation method may influence the dispersion of the active metal (cobalt) and hence the catalytic activity, but as the Fischer-Tropsch reaction is believed to be non-structure sensitive, dispersion should not influence the selectivity

The impregnated catalyst is dried, typically at 80-120 °C, to remove water from the catalyst pores, and then calcined at typically 200-450°C, e.g. at 300°C for 2-16h.

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#### **Catalyst testing**

One critical step before testing is the activation of the catalyst that involves reduction of cobalt oxide(s) to cobalt metal. This reduction can be performed by flowing a suitable reductive gas over the catalyst particles. Particularly suitable are hydrogen or carbon monoxide or mixtures thereof. The reductive gas can be mixed with inerts like nitrogen, noble gases or steam and suitable temperatures and pressures should be applied. If a fluidised bed reactor is used for activation, it may be convenient to use a recycle of (part of) the reductive gas and a slight atmospheric total overpressure in order to achieve a suitable gas flow. It is also possible to use elevated total pressures, eg. up to 8 bar or higher, or even the Fischer-Tropsch reactor pressure. Selection of the reduction temperature strongly depends on the actual catalyst formulation, in particular on the presence and nature of promoters. It is well known that Re is highly efficient as a promoter in achieving high reducibilities at a conveniently reduced temperature.

Some fixed-bed testing of activated catalysts has been performed in a laboratory unit with four parallel fixed-bed reactors. About 1 g of catalyst particles in a controlled size fraction was mixed with 5 times the volume of inert SiC. Reduction was performed in situ with hydrogen before an approximate 2:1 mixture of hydrogen and CO was carefully added. After 20 h on stream at 210°C and 20 bar total pressure, the space velocity was adjusted to give an estimated conversion level of CO after 90 h of between 45 and 50 %. It is of utmost importance to perform selectivity comparisons, as well as activity



comparisons, at the same conversion level, since the level of steam generated in the reaction has a profound influence on catalyst performance.

Table 3. Catalyst performance in the Fischer-Tropsch reaction.

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Modified alumina support Al-2 [metal impr. wt% /calc. Temp. °C]	Catalyst impregnation. Composition [wt%/wt%]	Relative activity	Relative C <sub>5+</sub> selectivity	Attrition resistance of support
---/500	20Co/0,5Re	1,54	0,933	Good
---/900	20Co/0,5Re	1,46	0,930	Good
---/1100	20Co/0,5Re	1,53	0,945	
---/1130	20Co/1Re	1,02	0,991	Low
---/1140	20Co/0,5Re	0,75	0,988	Very low
---/1140	20Co/0,25Re	0,83	0,972	Very low
5Co/900	20Co/0,5Re	1,68	0,938	Good
5Co/900	20Co	1,27	0,914	Good
5Co/1050	20Co/0,5Re	1,56	0,950	Good
5Co/1050	20Co	1,10	0,945	Good
10Co/900	20Co/0,5Re	1,50	0,941	Good
10Co/900	20Co	1,14	0,927	Good
10Co/1050	20Co/0,5Re	1,37	0,961	Good
10Co/1050	20Co	0,82	0,956	Good
20Co/900	20Co/0,5Re	1,73	0,952	Acceptable
---/500	12Co/0,5Re	0,92	0,931	Good
---/1130	12Co/1Re	1,05	0,987	Low

---/1140	12Co/1Re	0,66	1,007	Very low
5Co/1100	12Co/0,5Re	0,91	0,985	Low
10Co/1100	12Co/0,5Re	0,83	0,989	Good
10Co/1140	12Co/0,5Re	0,69	0,990	Acceptable
10Co/1140	12Co	0,54	0,977	Acceptable
20Co/1140	12Co/0,5Re	0,44	0,986	Very good
10Al/1050	20Co/0,5Re	1,37	0,953	Good
10Al/1050	20Co	0,58	0,946	Good
10Zn/1120	24Co/1Re	1,32	0,974	Low
10Zn/900	20Co/0,5Re	1,48	0,922	
10Zn/1120	12Co/0,5Re	0,95	0,975	Low
10Zn/1140	12Co/0,5Re	0,86	0,987	Acceptable
10Zn/1140	12Co/0,25Re	0,84	0,979	Acceptable
10Zn/1140	12Co	0,68	0,963	Acceptable
10Zn/1160	12Co/0,5Re	0,82	0,985	Acceptable
12,5Zn/1140	12Co/0,25Re	0,67	0,977	Good
15Zn/1140	12Co/0,5Re	0,76	0,984	Very good
10Mg/1140	24Co/1Re	0,64	0,932	Extremely good
5 Mg/1140	12Co/0,5Re	0,48	0,979	Very good
10Mg/1120	12Co/0,5Re	0,53	0,954	
10Mg/1140	12Co/0,5Re	0,38	0,952	Extremely good
10Mg/1160	12Co/0,5Re	0,25	0,928	
5Mg+5Zn/1140	12Co/0,5Re	0,44	0,972	Extremely good
3Ni/1140	12Co/0,5Re	0,66	0,991	Acceptable

5Ni/1140	12Co/0,5Re	0,89	0,989	Very good
5Ni/1150	12Co/0,5Re	0,87	0,980	
5Ni/1160	12Co/0,5Re	0,75	0,992	
5Ni/1170	12Co/0,5Re	0,62	0,983	
5Ni/1180	12Co/0,5Re	0,66	0,992	Very good
5Ni*/1140	12Co/0,25Re	0,73	0,970	Very good
7,5Ni*/1120	12Co/0,5Re	1,04	0,957	Extremely good
7,5Ni/1140	12Co/0,25Re	0,74	0,965	Very good
10Ni/900	12Co/0,5Re	1,48	0,906	
10Ni/1140	12Co/0,25Re	0,78	0,973	Extremely good

\*On Al-1 type alumina.

In Table 3 the first column relates to the first impregnation and calcination, showing the impregnated metal (with "---" indicating no impregnation) and the temperature of calcination. The second column relates to the second  
5 impregnation (with cobalt) and calcination, showing the cobalt and rhenium contents. Calcination was carried out at about 300°C.

From Table 3 it is clear that heat treatment of the Al-2 support at 900 °C or  
10 above, and particularly above 1100 °C, increases the selectivity of the catalyst, as also described in the present Applicants' WO 02/47816. It would seem that the same effect is seen for all modified aluminas that have been impregnated with a metal solution and then high temperature treated before standard impregnation and calcination. It should also be noted that the addition of  
15 Rhenium gives improved activity and selectivity for all catalysts in accordance with previous reports. Thus the present invention means that it now is possible to combine high selectivity with high strength of the catalyst particles.

There are, however, some differences between the 2-valent modifiers that have been applied. As it is desirable to use as little modifier as possible, values can e.g. be compared for the same wt% of the added 2-valent modifier before calcination at 1140 °C. First it can be noted that at the 10 wt% level only magnesium and nickel is able to give an attrition classified as "good" or better, and that this classification even is maintained for a 5 wt% loading. However, magnesium gives a clearly inferior catalytic performance, whereas 5 wt% nickel shows excellent activity and selectivity. A particular feature can be observed in the pore size distribution diagram of the catalysts (Figure 2), or the modified supports, plotted as differential pore volume as a function of pore diameter from the BET measurements with nitrogen. The pore size distribution of the Al-2 is bimodal, but the degree of bimodality decreases with calcination temperature of the modified support, concurrent with enhancement of strength and C5+ selectivity.

Figure 1 shows the effect of Ni loading and calcination temperature on the strength of modified Al-2 supports.

Figure 2 shows temperature effect on the pore size distribution of catalysts employing the modified catalyst supports, prepared by high temperature calcination of 5 wt% Ni as nickel nitrate impregnated on  $\gamma$ -alumina.

Claims

1. A method of producing an alumina-supported catalyst, which comprises the following steps: a first impregnation step in which an initial alumina support material is impregnated with a source of a 2-valent metal capable of forming a spinel compound with alumina;  
a first calcination step in which the impregnated alumina support material is calcined at a temperature of at least 550°C to produce a modified alumina support material;  
a second impregnation step in which the modified alumina support material is impregnated with a source of catalytically active metal;  
and a second calcination step in which the impregnated modified support material is calcined at a temperature of at least 150°C.
2. A method as claimed in Claim 1, in which the initial alumina support material at least predominantly comprises  $\gamma$ -alumina.
3. A method as claimed in Claim 1 or Claim 2, in which the impregnated modified support material is calcined at a temperature of up to 600°C.
4. A method as claimed in any preceding claim, in which the impregnated and calcined modified support has a pore volume measured by nitrogen BET in which at least half the pore volume is constituted by pores larger than 30 nm in diameter.
5. A method as claimed in any preceding Claim, in which the initial alumina support material has a specific surface area in the range 100 to 300 m<sup>2</sup>/g.
6. A method as claimed in any preceding Claim, in which the initial

alumina support material comprises essentially spherical particles having a particle size range whereby at least 80 volume % fall in the range 25 to 150  $\mu\text{m}$ .

- 5      7.    A method as claimed in any preceding Claim, in which the initial alumina support material has a pore volume greater than  $0.2\text{cm}^3/\text{g}$ , preferably greater than  $0.4\text{cm}^3/\text{g}$ .
- 10     8.    A method as claimed in any preceding Claim, in which the first calcination step is carried out at a temperature in the range 800 to  $1200^\circ\text{C}$ .
9.    A method as claimed in any preceding Claim, in which the first calcination step is carried out at a temperature in the range 900 to  $1200^\circ\text{C}$ .
- 15     10.   A method as claimed in any preceding Claim, in which the modified alumina support has a surface area of less than  $40\text{ m}^2/\text{g}$ .
11.   A method as claimed in any preceding Claim, in which the modified alumina support has an ASTM attrition value of less than 20 % by weight of  
20     fines produced by 5 hours testing
12.   A method as claimed in any preceding Claim, in which the modified alumina support has an ASTM attrition value of less than 8 % by weight of  
fines produced by 5 hours testing
- 25     13.   A method as claimed in any preceding Claim, in which the modified alumina support comprises at least 10 % by weight of alfa-alumina.
14.   A method as claimed in any preceding Claim, in which the source of a

2-valent metal comprises a source of cobalt, zinc, magnesium, manganese, nickel or iron.

15      15.    A method as claimed in any preceding Claim, in which the source of a  
5      2-valent metal does not comprise a source of cobalt.

16.    A method as claimed in any preceding Claim, in which the source of a  
2-valent metal comprises nickel.

10      17.    A method as claimed in any preceding Claim, in which the source of a  
2-valent metal comprises nickel in an amount of less than 20 wt% of the final  
reduced catalyst.

15      18.    A method as claimed in any preceding Claim, in which the source of a  
2-valent metal comprises nickel in an amount of less than 8 wt% of the final  
reduced catalyst.

20      19.    A method as claimed in any preceding Claim, which includes  
additionally impregnating or co-impregnating the alumina support material  
with a promoter.

20.    A method as claimed in Claim 19, in which the promoter comprises  
platinum or rhenium.

25      21.    A method as claimed in Claim 20, in which the promoter is rhenium and  
the source of rhenium is selected from perrhenic acid ( $\text{HReO}_4$ ), ammonium  
perrhenate, rhenium halide(s) and rhenium carbonyl(s).

22.    A method as claimed in any preceding Claim, which includes

additionally incorporating a stabiliser into the alumina support material with a stabiliser.

23. A method as claimed in Claim 22, in which the stabiliser comprises  
5 lanthanum.

24. A method as claimed in any preceding Claim, in which the first  
impregnation step comprises an incipient wetness treatment in which an  
aqueous solution of the 2-valent metal compound is mixed with the dry support  
10 material until the pores are filled, and the impregnated support is then dried,  
prior to the first calcining step.

25. A method as claimed in any preceding Claim, in which the source of  
catalytically active metal comprises a source of cobalt.  
15

26. A method as claimed in Claim 25, in which the source of cobalt is  
selected from cobalt nitrate ( $\text{Co}(\text{NO}_3)_2$ ), cobalt acetate(s), cobalt halide(s),  
cobalt carbonyl(s), cobalt oxalate(s), cobalt phosphate(s), cobalt carbonate(s),  
cobalt (hexa)amine salt(s) and organic cobalt compounds.  
20

27. A method as claimed in Claim 25 or Claim 26, in which the second  
impregnation step comprises an incipient wetness treatment in which an  
aqueous solution of a cobalt compound and optionally a rhenium compound is  
mixed with the modified support material until the pores are filled and the  
25 impregnated modified support material is then dried, prior to the second  
calcination step.

28. A method as claimed in Claim 24 or Claim 26 or Claim 27, in which the  
amount of aqueous solution used in the impregnation is 0.05-2 times larger



than the measured pore volume of the catalyst support.

29. A method as claimed in Claim 24 or any of Claims 26 to 28, in which drying is carried out at 80 to 120°C.

5

30. A method as claimed in any preceding Claim, in which, after the second calcination step, the alumina-supported catalyst material is activated.

31. A method as claimed in Claim 30, in which the activation step  
10 comprises reduction of a substantial portion of the catalytically active metal compound present to the metal.

32. A method as claimed in Claim 31, in which the reduction is carried out by treating the catalyst material with a reducing gas.

15

33. A method as claimed in Claim 32, in which the reducing agent is hydrogen and/or carbon monoxide, optionally mixed with an inert gas.

34. A method as claimed in any of Claims 31 to 33, in which the reduction  
20 is carried out at an activation temperature of 250 to 500°C.

35. A method as claimed in Claim 34, in which the activation temperature is in the range 300 to 450°C.

25 36. A method as claimed in any preceding Claim, in which, prior to impregnation, the alumina support has an ASTM attrition value of less than 30% by weight of fines produced by 5 hours testing.

37. A method as claimed in Claim 36 in which the ASTM value is less than

20%.

38. A catalyst material produced by a method as claimed in any preceding Claim.

5

39. A catalyst as claimed in Claim 38, in which the catalytically active metal and optionally the 2-valent metal are cobalt, and the cobalt content of the catalyst is from 10 to 40% by weight.

10

40. A catalyst as claimed in Claim 39, in which the cobalt content is from 15 to 25% by weight.

41. A catalyst as claimed in any of Claims 38 to 40, incorporating less than 3% by weight of a promoter.

15

42. A catalyst as claimed in Claim 41, in which the promoter is rhenium or platinum.

43. A catalyst as claimed in any of Claims 38 to 42, in which the initial support material predominantly comprises  $\gamma$ -alumina .

20

44. A catalyst as claimed in Claim 43, in which the  $\gamma$ -alumina is stabilised with a stabilising agent, optionally lanthanum.

45. A catalyst as claimed in any of Claims 38 to 44, in which the alumina support material includes a binder.

25

46. A catalyst as claimed in Claim 45, in which the binder represents less

than 25% by weight of the catalyst.

47. A catalyst as claimed in Claim 45 or Claim 46, in which the binder is an alumina-containing binder material.

5

48. A catalyst as claimed in any of Claims 38 to 47, in which the specific surface area of the prepared catalyst, comprising the cobalt on the modified support, is up to  $150 \text{ m}^2/\text{g}$ .

10

49. A catalyst as claimed in any of Claims 37 to 48, in which the pore volume of the prepared catalyst is from  $0.05$  to  $0.7 \text{ cm}^3/\text{g}$ .

50. A catalyst as claimed in any of Claims 37 to 49, in which the pore diameter of the prepared catalyst is at least  $10 \text{ nm}$ , preferably at least  $18 \text{ nm}$ .

15

51. The use of a catalyst as claimed in any of Claims 48 to 50 in a Fischer-Tropsch synthesis reaction.

20

52. A use as claimed in Claim 51, in which the reaction is carried out in a slurry bubble column reactor.

25

53. A use as claimed in Claim 52, in which  $\text{H}_2$  and  $\text{CO}$  are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the  $\text{H}_2$  and  $\text{CO}$ , the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

54. A process for the production of hydrocarbons which comprise subjecting  $\text{H}_2$  and  $\text{CO}$  gases to a Fischer-Tropsch synthesis reaction in a reactor in the

presence of a catalyst as claimed in any of Claims 28 to 40.

55. A process as claimed in Claim 54, in which the reaction is a three-phase reaction in which the reactants are gaseous, the product is at least partially liquid and the catalyst is solid.

56. A process as claimed in Claim 55, in which the reaction is carried out in a slurry bubble column reactor.

57. A process as claimed in Claim 56, in which the H<sub>2</sub> and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H<sub>2</sub> and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

58. A process as claimed in any of Claims 54 to 57, in which the reaction temperature is in the range 190-250°C.

59. A process as claimed in Claim 58, in which the reaction temperature is in the range 200-230°C.

60. A process as claimed in any of Claims 54 to 59, in which the reaction pressure is in the range 10-60 bar.

61. A process as claimed in Claim 60, in which the reaction pressure is in the range 15 to 30 bar.

62. A process as claimed in any of Claims 54 to 61, in which the H<sub>2</sub>/CO ratio of the gases supplied to the Fischer-Tropsch synthesis reactor is in the

range 1.1 to 2.2.

63. A process as claimed in Claim 62, in which the  $H_2/CO$  ratio is in the range 1.5 to 1.95.

5

64. A process as claimed in any of Claims 54 to 63, in which the superficial gas velocity in the reactor is in the range 5 to 60 cm/s.

65. A process as claimed in Claim 64 in which the superficial gas velocity is  
10 in the range 20 to 40 cm/s.

66. A process as claimed in any of Claims 54 to 65, in which the product of the Fischer-Tropsch synthesis reaction is subsequently subjected to post-processing.

15

67. A process as claimed in Claim 66 in which the post-processing is selected from de-waxing, hydro-isomerisation, hydro-cracking and combinations of these.

20 68. A method for the production of an alumina support for a catalyst, which comprises impregnating an initial alumina support material with a source of a 2-valent metal capable of forming a spinel compound with alumina, and calcining the impregnated alumina at a temperature of at least 550°C.

25 69. A method as claimed in Claim 68, in which the initial alumina support material at least predominantly comprises  $\gamma$ -alumina.

70. A method as claimed in Claim 68 or Claim 69, in which the initial alumina support material has a specific surface area in the range 100 to 300

m<sup>2</sup>/g.

71. A method as claimed in any of Claims 68 to 70, in which the initial alumina support material comprises agglomerated essentially spherical particles having a particle size range whereby at least 80% fall in the range 30 to 120 µm.

72. A method as claimed in any of Claims 68 to 71, in which the initial alumina support material has a pore volume greater than 0.2cm<sup>3</sup>/g, preferably greater than 0.4cm<sup>3</sup>/g.

73. A method as claimed in any of Claims 68 to 72, in which the impregnated alumina support material is calcined at a temperature in the range 800 to 1200°C.

74. A method as claimed in any of Claims 68 to 73, in which the source of a 2-valent metal comprises a source of cobalt, zinc or magnesium.

75. A method as claimed in any of Claims 68 to 74, which includes additionally impregnating the alumina support material with a promoter.

76. A method as claimed in Claim 75, in which the promoter comprises platinum or rhenium.

77. A method as claimed in Claim 76, in which the promoter is rhenium and the source of rhenium is selected from perrhenic acid (HReO<sub>4</sub>), ammonium perrhenate, rhenium halide(s) and rhenium carbonyl(s).

78. A method as claimed in Claim 77, in which the source of the 2-valent

metal compound is cobalt nitrate and the rhenium compound is perrhenic acid.

79. A method as claimed in Claim 68 to 78, which includes additionally impregnating the alumina support material with a stabiliser.

5

80. A method as claimed in Claim 79, in which the stabiliser comprises lanthanum.

81. A method as claimed in any one of Claims 68 to 80, in which the first  
10 impregnation step comprises an incipient wetness treatment in which an aqueous solution of the 2-valent metal compound and optionally a rhenium compound is mixed with the dry support material until the pores are filled, and the impregnated support is then dried, prior to the second calcining step.

15 82. A method as claimed in any of Claims 68 to 81, in which the amount of aqueous solution used in the impregnation is 0.05-2 times larger than the measured pore volume of the catalyst support.

20 83. A method as claimed in any of Claims 81 to 82, in which the drying is carried out at 80 to 120°C.

1/1

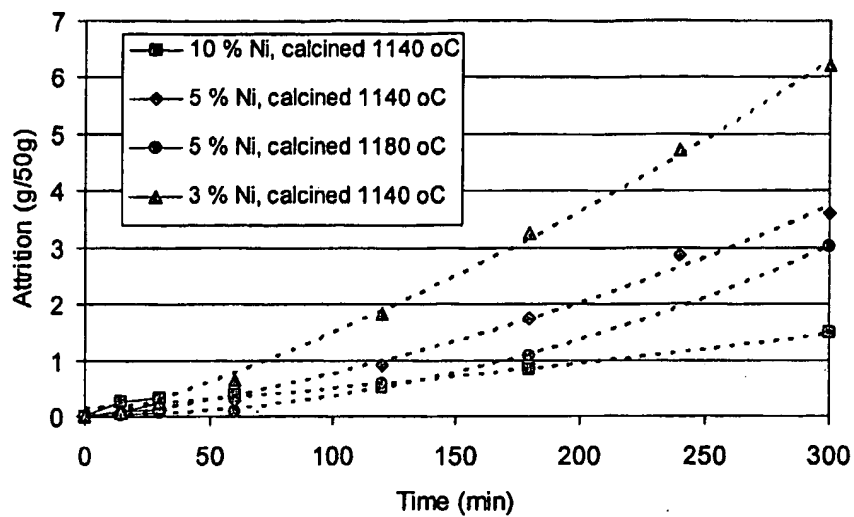


Fig 1

Catalyst (12Co/0.0%Re) on modified support:  
5% Ni on Al-2

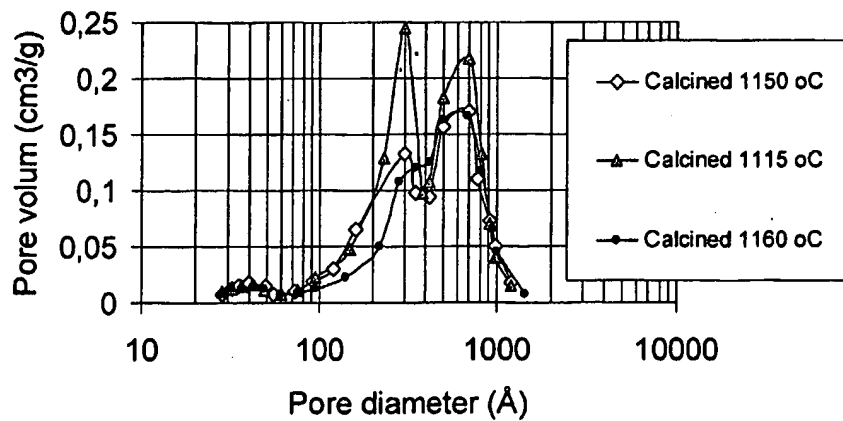


Fig 2



# INTERNATIONAL SEARCH REPORT

Inte al Application No  
PCT/GB2005/000287

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/75 B01J23/755 B01J23/889 B01J23/89 B01J35/00  
B01J37/02 C07C1/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 3 933 883 A (PARTHASARATHY ET AL) 20 January 1976 (1976-01-20)</p> <p>column 2, line 38 - column 3, line 7 example 1</p> <p style="text-align: center;">----- -/--</p>	<p>1-12, 14-19, 24-38, 43, 45-50, 54,55, 68-75, 81-83</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

3 May 2005

Date of mailing of the international search report

18/05/2005

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# INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/GB2005/000287

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